

(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開平7-81932

(43) 公開日 平成7年(1995)3月28日

(51) Int.Cl. ⁸	識別記号	庁内整理番号	F I	技術表示箇所
C 0 1 F 17/00	A	9040-4G		
// B 0 1 J 23/10	Z A B A	8017-4G		

審査請求 未請求 請求項の数 1 O L (全 5 頁)

(21) 出願番号 特願平5-229072

(22) 出願日 平成5年(1993)9月14日

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(54) 【発明の名称】 酸化第二セリウムの製造方法

(57) 【要約】

【目的】 高い比表面積であり、高温での比表面積の低下が少なく安定しているもので、更に色調を白色に近づけた酸化第二セリウムを提供する。

【構成】 炭酸セリウムを特殊な条件にて加湿加熱処理し、モノオキシ炭酸セリウムを得た後、それを焼成し酸化第二セリウムを製造する方法。

【特許請求の範囲】

【請求項1】 炭酸セリウムを相対湿度80%以上の高湿度下で、60～100℃の温度範囲にて加湿加熱処理を行ないモノオキシ炭酸セリウムにした後、焼成することを特徴とする酸化第二セリウムの製造方法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、酸化第二セリウムの製造方法に関し、詳しくは、高温領域でも比表面積の低下が少なく安定した酸化第二セリウムおよび色調として白色に近い酸化第二セリウムを提供することに関する。

【0002】

【従来の技術】従来、酸化第二セリウムは、排ガス清浄用触媒、シリコンゴムフィラー、研磨材等として大量に使用されており、例えば触媒分野においては、酸化雰囲気で酸素を吸収し、還元雰囲気で酸素を放出するという酸化第二セリウムの特性を利用して、HC、CO、NO_xに対する浄化率の向上等が行なわれており、またシリコンゴムフィラーにおいてはゴム強度を低下させることなく耐熱性を向上させる添加剤として利用されている。このような従来の酸化第二セリウムは、通常、例えばセリウムの硝酸塩溶液または塩酸塩溶液に、稀酸若しくは重炭酸アンモニウムを添加し、得られる沈殿物を分別、洗浄、乾燥および焼成する方法等により製造されている。しかしながら、前記方法等により製造された従来の酸化第二セリウムは、100m²/g程度の比表面積を有するものの、800℃焼成で比表面積が10m²/g以下に低下する、更にシリコンゴムに添加して使用する際、酸化第二セリウムの黄色度が高いため、ゴムの色が黄色っぽくなるという欠点を有していた。また、研磨材に用いられている酸化第二セリウムの研磨能力はメカノケミカルな部分（表面活性）に大きく左右されるため、通常の800～1000℃程度の焼成温度域での高比表面積化が望まれている。

【0003】

【発明が解決しようとする課題】上記のような用途に用い、更に性能等を向上させるため、酸化第二セリウムの特性として、更に高い比表面積、高温での比表面積の低下が少なく安定しているもの並びに色調を白色に近づけることが要求されている。

【0004】

【課題を解決するための手段】本発明者は上記の課題を解決すべく種々検討した結果、炭酸セリウムを相対湿度80%以上の高湿度下で、60～100℃の温度範囲にて加湿加熱処理を行ないモノオキシ炭酸セリウムにした後、焼成することを特徴とする酸化第二セリウムの製造方法を見出した。

【0005】まず、原料である炭酸セリウムについて記す。炭酸セリウムは市販されており、それを使用することも本発明ではできる。炭酸セリウムを製造する一例を

示すとする以下になる。即ち、まず硝酸セリウム水溶液と、重炭酸アンモニウム水溶液とを混合し、炭酸セリウム沈殿物を得る。この際混合順序は、硝酸セリウム水溶液に、重炭酸アンモニウム水溶液を添加しても、また重炭酸アンモニウム水溶液に硝酸セリウム水溶液を添加混合しても良い。該硝酸セリウム水溶液の濃度は、好ましくは30～200g/リットル、特に好ましくは100～150g/リットルの範囲である。また硝酸セリウム水溶液と重炭酸アンモニウム水溶液との混合割合は、各水溶液中に含有される硝酸セリウムおよび重炭酸アンモニウムの重量比で1:1.4～3の範囲であるのが好ましい。この際得られる炭酸セリウムは、3価のセリウムでCe₂(CO₃)₃・xH₂O (x=1～8)である。

【0006】本発明では次に、上記のようにして得られた炭酸セリウムや市販のものを60～100℃の温度範囲にて相対湿度80%以上の高湿度下にて加湿加熱処理を行なう。この処理により、六角板状の炭酸セリウムから針状ないしは球状のモノオキシ炭酸セリウム[Ce₂O(CO₃)₂・xH₂O (x=1～6)]が生成する。

【0007】上記加湿加熱処理は、恒温恒湿器やスチームを導入した乾燥器等により行なうことができ、その処理時間は、1時間以上が望ましい。加湿乾燥処理の温度が60℃未満の場合には、結晶水が脱離し難いためか、モノオキシ炭酸セリウムが生成せず、100℃を越えると結晶水の脱離前に、表面水分の脱離が生じるためか、モノオキシ炭酸セリウムの生成割合が低下し、大半がCe(OH)(CO₃)₂・xH₂O等の塩基性炭酸塩となるため、上記温度範囲とする必要がある。また、相対湿度が80%未満だと、結晶水の脱離前に表面水分が脱離するためか、通常の乾燥処理と同様に炭酸セリウムから非晶質部分が現われてきてしまうため好ましくない。

【0008】次に、生成させたモノオキシ炭酸セリウムを焼成することにより酸化第二セリウムが得られるが、この焼成温度は300～650℃が好ましく、より好ましくは300～550℃で、焼成時間は1～4時間が好ましい。焼成温度が300℃未満の場合には焼成時間を長くしても完全にCe₂O₃に変化し難く、550℃を越えると得られたCe₂O₃の比表面積が比較的に小さいので望ましくない。

【0009】本発明にて得られる酸化第二セリウムは、140m²/g以上と比表面積が大きく、また高温、特に700℃以上でも比表面積の低下が少ない特性を有し、白色度の高い色調のものである。また、その形状も針状、球状、立方体等であり、球状、立方体の場合、それぞれ径、一辺が20μm以下であり、針状の場合太さが10μm以下、長さが60μm、アスペクト比が3以上が普通であるが、この値に限定されるものではない。本発明の製造法により得られる酸化第二セリウムは、そのままでも使用することもできるが、排ガス清浄用触媒

に用いる場合には酸化ジルコニウム、酸化アルミニウム、アルカリ土類金属酸化物と混合したり、シリコンゴムフィラーに用いる場合には二酸化チタン、酸化アルミニウム等と混合し、研磨材に用いる場合には、希土類金属酸化物およびフッ化物や酸化アルミニウム、酸化ジルコニウムといった通常の研磨材と混合して用いることもできる。

【0010】

【実施例】以下に実施例および比較例にて詳説する。

実施例1

高純度硝酸セリウム溶液(東北金属化学株式会社製、純度99.95%)を水に溶解し、35℃にて、酸化第二セリウム Ce_2O_3 、換算で50g/リットルの硝酸セリウム水溶液1リットルに、濃度150g/リットルの重炭酸アンモニウム水溶液1リットルを添加混合し、六角板状の炭酸セリウムの沈殿物として2300g得た。得られた沈殿物を恒温恒湿器に入れ、85℃にて、相対湿度95%下で8時間加湿乾燥処理をし、針状のモノオキシ炭酸セリウム $\text{Ce}_2\text{O}(\text{CO}_3)_2 \cdot \text{H}_2\text{O}$ 1700gを得た。これを400℃で2時間焼成し酸化第二セリウムを得た。得られた酸化第二セリウムの特性および該酸化第二セリウムを800℃で5時間再焼成し比表面積の変化した値を表1に示す。

【0011】なお、表1中に示した黄色度(YI値)は以下のようにして測定した値である。黄色度とは白色から黄方向に離れる度合いを示すもので、理想的な白色は黄色度がほぼ0となる。黄色さが増して、理想的な白色から遠ざかるに従って、黄色度の数値が大きくなる。黄色度の測定に際し、得られた焼成物をナイロンボット(ナイロンボール)で約2時間解砕し、平均粒径 $d_{50}=2.0 \pm 0.2 \mu\text{m}$ で22 μm 以下の粉末にする。この解砕粉約5gを東京電色(株)製、色差計にて丸セル(30mmφ×

*×15t)に無加圧にて詰め測定し、XYZの各値を測り、ASTM E 313に準じYI値(黄色度)を求めた。表1に示したYI値は一サンプルにつき3回、上記操作を繰り返し、各3回測定し計9回の平均値にて表示した。

【0012】比較例1

実施例1において炭酸セリウムの沈殿物を加湿乾燥処理せず、直接400℃で2時間焼成し酸化第二セリウムを得た。それ以外の条件は実施例1と同一である。得られた酸化第二セリウムの特性および800℃、5時間再焼成での比表面積値を表1に示す。

【0013】比較例2

実施例1で得られた六角板状の炭酸セリウムの沈殿物をオートクレーブに入れ、120℃にて8時間水熱処理を行なった。得られた生成物の主なものは、六角板状と球状の塩基性炭酸セリウム $\text{Ce}(\text{OH})(\text{CO}_3) \cdot 2\text{H}_2\text{O}$ で、モノオキシ炭酸セリウムの生成量は全体の5%程度であった。この混合物を400℃で2時間焼成し、表1に示す酸化第二セリウムを得た。また、この800℃で5時間再焼成した後の比表面積値も表1に示す。

【0014】比較例3

実施例1で得られた六角板状の炭酸セリウムの沈殿物をスチームを導入の恒温恒湿器に入れ、50℃で相対湿度95%にて8時間加湿加熱処理を行なった。その結果、モノオキシ炭酸セリウムは得られず、六角板状の炭酸セリウムのままであった。これを400℃で2時間焼成し、表1に示す酸化第二セリウムを得て、更に800℃で5時間再焼成し比表面積の変化を求めた。

【0015】

【表1】

	400℃×2時間焼成後		800℃×5時間再焼成後
	比表面積(m^2/g)	YI値	比表面積(m^2/g)
実施例1	153	21	15.2
比較例1	112	32	2.7
比較例2	112	31	2.8
比較例3	121	28	5.7

【0016】実施例2

重炭酸アンモニウム水溶液に、硝酸セリウム水溶液を添加混合した以外は、実施例1と同一条件にて六角板状の炭酸セリウムを得た。この沈殿物2300gをスチーム導入乾燥器にて、95℃で相対湿度95%にて8時間加湿加熱処理を行ない、針状のモノオキシ炭酸セリウム $\text{Ce}_2\text{O}(\text{CO}_3)_2 \cdot \text{H}_2\text{O}$ 1700gを得た。これを300℃で4時間焼成し、表2に示す特性の酸化第二セリ

ウムを得た。更にこれを800℃で5時間再焼成し比表面積の変化を求め、その値を表2に示す。

【0017】比較例4

実施例2で得た六角板状の炭酸セリウムの沈殿物を、加湿加熱処理をせず、直接300℃で4時間焼成し、表2に示す特性の酸化第二セリウムを得て、実施例2と同様の再焼成処理を行ない、表2の値に変化することが分った。

【0018】

* * 【表2】

	300℃×4時間焼成後		800℃×5時間再焼成後
	比表面積(m ² /g)	YI値	比表面積(m ² /g)
実施例2	161	24	13.6
比較例4	121	34	2.8

【0019】実施例3

実施例1と同様にして調製した六角板状の炭酸セリウムの沈殿物を恒温恒湿器に入れ、60℃、相対湿度90%において12時間加湿乾燥処理を行ない、針状のモノオキシ炭酸セリウム $\text{Ce}_2\text{O}(\text{CO}_3)_2 \cdot 3\text{H}_2\text{O}$ 1800gを得た。得られたモノオキシ炭酸セリウムを500℃で2時間焼成して得られた酸化第二セリウムの特性および該酸化第二セリウムを800℃で5時間再焼成した際の比表面積を表3に示す。

【0020】比較例5

※実施例1と同様にして調製した六角板状の炭酸セリウムの沈殿物を恒温恒湿器に入れ、60℃、相対湿度70%において12時間加湿乾燥処理を行なったが、モノオキシ炭酸セリウムは得られず、六角板状の炭酸セリウムのままであった。この炭酸セリウムを500℃で2時間焼成して得られた酸化第二セリウムの特性および該酸化第二セリウムを800℃で5時間再焼成した際の比表面積を表3に示す。

【0021】

* 【表3】

	500℃×2時間焼成後		800℃×5時間再焼成後
	比表面積(m ² /g)	YI値	比表面積(m ² /g)
実施例3	142	19	14.7
比較例5	103	28	3.1

【0022】実施例4

実施例2と同様にして調製した六角板状の炭酸セリウムの沈殿物をスチームを導入した乾燥器に入れ、85℃、相対湿度80%において8時間加湿乾燥処理を行ない、針状のモノオキシ炭酸セリウム1700gを得た。得られたモノオキシ炭酸セリウム $\text{Ce}_2\text{O}(\text{CO}_3)_2 \cdot \text{H}_2\text{O}$ を500℃で2時間焼成して得られた酸化第二セリウムの特性および酸化第二セリウムを800℃で5時間再焼成した際の比表面積を表4に示す。

【0023】比較例6

実施例2と同様にして調製した六角板状の炭酸セリウムの沈殿物をスチームを導入した乾燥器に入れ、85℃、相対湿度70%において8時間加湿乾燥処理を行なったが、モノオキシ炭酸セリウムは得られず、六角板状の炭酸セリウムのままであった。この炭酸セリウムを500℃で2時間焼成して得られた酸化第二セリウムの特性お★

★よび該酸化第二セリウムを800℃で5時間再焼成した際の比表面積を表4に示す。

【0024】比較例7

実施例2と同様にして調製した六角板状の炭酸セリウムの沈殿物を底部に水を張ったバットを置いた乾燥器に入れ、110℃、相対湿度85%相当の水蒸気圧において、8時間加湿乾燥処理を行なった。この際の主生成物は六角板状と球状の塩基性炭酸セリウム塩で、この他に20%程度の未反応の六角板状を保った炭酸セリウムが認められ、目的とするモノオキシ炭酸セリウムの生成量は全体の5%程度であった。得られた混合物を500℃で2時間焼成して得られた酸化第二セリウムの特性および該酸化第二セリウムを800℃で5時間再焼成した際の比表面積を表4に示す。

【0025】

【表4】

	500℃×2時間焼成後		800℃×5時間再焼成後
	比表面積(m ² /g)	YI値	比表面積(m ² /g)
実施例4	147	18	14.8
比較例6	96	27	2.7
比較例7	105	26	4.9

【0026】

【発明の効果】本発明にて得られる酸化第二セリウムは、従来の酸化第二セリウムに比較して

イ) 大きな比表面積を有する

ロ) 高温での比表面積の低下が少ない。

ハ) 白色に近い色調を呈する。

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等多くの効果がある。また、本発明の製造方法では、前記の特性を有する本発明の酸化第二セリウムを再現性良く、かつ容易に製造することができる。そのため、本発

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明で得られる酸化第二セリウムは、排ガス清浄用触媒、シリコーンゴムフィラー等のように耐熱安定性が要求される酸化第二セリウムに特に適する。

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 07-081932

(43)Date of publication of application : 28.03.1995

(51)Int.Cl.

C01F 17/00
// B01J 23/10

(21)Application number : 05-229072

(71)Applicant : SHOWA DENKO KK

(22)Date of filing : 14.09.1993

(72)Inventor : MATSUKURA MINORU

(54) PRODUCTION OF CERIC OXIDE

(57)Abstract:

PURPOSE: To easily obtain the white tone ceric oxide having high specific surface area, low in reduction of the specific surface area under high temp. by baking monooxy cerium carbonate obtained by subjecting to moisture and heat treatment cerium carbonate.

CONSTITUTION: Cerium carbonate is put in a constant temp.constant humidity vessel or the drying vessel, etc., introduced steam, and is subjected to moisten and heat-treatment within the temp. range of 60-100°C, under the high humidity of $\geq 80\%$ relative humidity and for ≥ 1 hour, and acicular or spherical monooxy cerium carbonate is obtained. Then, the monooxy cerium carbonate is burnt at 300-650°C for 1-4 hour to produce the ceric oxide having $\geq 140\text{m}^2/\text{g}$ specific surface area.

LEGAL STATUS

[Date of request for examination] 18.05.2000

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number] 3440505

[Date of registration] 20.06.2003

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

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CLAIMS

[Claim(s)]

[Claim 1] The manufacture approach of the second cerium of oxidation characterized by calcinating after performing humidification heat-treatment in a 60-100-degree C temperature requirement and using a carbonic acid cerium as a mono-oxy-carbonic acid cerium under high humidity of 80% or more of relative humidity.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to offering in detail the second cerium of oxidation by which the fall of specific surface area was stabilized few also in the high temperature field, and the second cerium of oxidation near white as a color tone about the manufacture approach of the second cerium of oxidation.

[0002]

[Description of the Prior Art] Conventionally, the second cerium of oxidation is used in large quantities as the catalyst for exhaust gas clarification, a silicone rubber filler, abrasives, etc., for example, is set in the catalyst field. Absorb oxygen by the oxidizing atmosphere and the property of the second cerium of oxidation of emitting oxygen by reducing atmosphere is used. HC, CO, and NO_x It is used as an additive which raises thermal resistance, without performing receiving improvement in the rate of purification, and reducing rubber reinforcement in a silicone rubber filler. Such second conventional cerium of oxidation is manufactured by the approach of adding oxalic acid or ammonium bicarbonate in the nitrate solution or hydrochloride solution of a cerium, and usually washing, drying and calcinating the precipitate obtained a RO exception etc. However, although the second conventional cerium of oxidation manufactured by said approach etc. had the specific surface area about 100m² / g, when [in which specific surface area falls to below 10m² / g by 800 degree-C baking] adding and using it for silicone rubber further, since whenever [yellow / of the second cerium of oxidation] was high, it had the fault that the color of rubber came seemingly to be yellow. Moreover, since the polish capacity of the second cerium of oxidation used for abrasives is greatly influenced by the mechanochemical part (surface activity), high specific-surface-area-ization in the about 800-1000-degree C usual burning-temperature region is desired.

[0003]

[Problem(s) to be Solved by the Invention] In order to use for the above applications and to raise the engine performance etc. further, it is required that a color tone should be brought close to white at the thing list whose fall of a still higher specific surface area and the specific surface area in an elevated temperature is stable few as a property of the second cerium of oxidation.

[0004]

[Means for Solving the Problem] As a result of examining many things that the above-mentioned technical problem should be solved, after this invention person performed humidification heat-treatment in the 60-100-degree C temperature requirement and used the carbonic acid cerium as the mono-oxy-carbonic acid cerium under high humidity of 80% or more of relative humidity, he found out the manufacture approach of the second cerium of oxidation characterized by calcinating.

[0005] First, it describes about the carbonic acid cerium which is a raw material. The carbonic acid cerium is marketed and it can also perform using it in this invention. It is as follows supposing an example which manufactures a carbonic acid cerium is shown. That is, a cerium-nitrate water solution and an ammonium bicarbonate water solution are mixed first, and carbonic acid cerium precipitate is obtained. Under the present circumstances, a mixed sequence foreword may add an ammonium bicarbonate water solution in a cerium-nitrate water solution, or may carry out addition mixing of the cerium-nitrate water solution at an ammonium bicarbonate water solution. 30-200g / of concentration of this cerium-nitrate water solution is [1.] the range of 100-150g/l. especially preferably preferably. Moreover, as for the mixed rate of a cerium-nitrate water solution and an ammonium bicarbonate water solution, it is desirable that it is the range of 1:1.4-3 in the weight ratio of

the cerium nitrate contained in each water solution and ammonium bicarbonate. Under the present circumstances, the carbonic acid ceriums obtained are $\text{Ce}_2\text{O}_3(\text{CO}_3)$ and $x\text{H}_2\text{O}$ ($x=1-8$) in a trivalent cerium. [0006] This invention next performs humidification heat-treatment for the carbonic acid cerium obtained as mentioned above or a commercial thing under high humidity of 80% or more of relative humidity in a 60-100-degree C temperature requirement. By this processing, a needlelike or spherical mono-oxy-carbonic acid cerium [$\text{Ce}_2\text{O}(\text{CO}_3)_2$ and $x\text{H}_2\text{O}$ ($x=1-6$)] generates from a 6 corner-guard-like carbonic acid cerium.

[0007] The oven which introduced a thermo hygostat and steam can perform the above-mentioned humidification heat-treatment, and the processing time has 1 desirable hours or more. Since the generation rate of a mono-oxy-carbonic acid cerium will fall probably because the desorption for surface water arises and most will serve as basic carbonates, such as $\text{Ce}(\text{OH})(\text{CO}_3)$ and $x\text{H}_2\text{O}$, before desorption of water of crystallization if a mono-oxy-carbonic acid cerium does not generate but 100 degrees C is exceeded probably because water of crystallization cannot **** easily when the temperature of humidification desiccation processing is less than 60 degrees C, it is necessary to consider as the above-mentioned temperature requirement. Moreover, since an amorphous part appears from a carbonic acid cerium like [if relative humidity is less than 80%, probably because the amount of surface water will **** before desorption of water of crystallization] the usual desiccation processing, it is not desirable.

[0008] Next, although the second cerium of oxidation is obtained by calcinating the mono-oxy-carbonic acid cerium made to generate, it is 300-550 degrees C more preferably, and 1 - 4 hours of firing time are desirable [this burning temperature has desirable 300-650 degrees C, and]. It is completely CeO_2 even if it lengthens firing time, when burning temperature is less than 300 degrees C. CeO_2 obtained when it was hard to change and 550 degrees C was exceeded Since specific surface area is small in comparison, it is not desirable.

[0009] The second cerium of oxidation obtained in this invention has more than $140\text{m}^2/\text{g}$, and a large specific surface area, and it has an elevated temperature and at least 700 degrees C or more of properties with especially few falls of specific surface area, and is the thing of the high color tone of a whiteness degree. Moreover, that configuration is also a needle, a globular shape, a cube, etc., in the case of a globular shape and a cube, a path and one side are 20 micrometers or less, respectively, and when needlelike, a size is not limited for them to this value, although 10 micrometers or less and die length have [three or more] 60 micrometers and a common aspect ratio. Even if it remains as it is, it can also be used, but in mixing with a zirconium dioxide, an aluminum oxide, and alkaline-earth-metal oxide in using for the catalyst for exhaust gas clarification, or using for a silicone rubber filler, it mixes with a titanium dioxide, an aluminum oxide, etc., and it can mix with the usual abrasives, such as rare earth metal oxide and a fluoride, an aluminum oxide, and a zirconium dioxide, and the second cerium of oxidation obtained according to the manufacturing method of this invention can also be used, when using for abrasives.

[0010]

[Example] It explains in full detail in an example and the example of a comparison below.

An example 1 high-grade cerium-nitrate solution (northeast metalization study incorporated company make, 99.95% of purity) is dissolved in water, and it is the second cerium CeO_2 of oxidation at 35 degrees C. By conversion, in 1l. of 50g [/l.] cerium-nitrate water solutions, addition mixing of the 1l. of the ammonium bicarbonate water solutions with a concentration of 150g [/l.] was carried out, and 2300g was obtained as precipitate of a 6 corner-guard-like carbonic acid cerium. The obtained precipitate was put into the thermo hygostat, at 85 degrees C, humidification desiccation processing was carried out under 95% of relative humidity for 8 hours, and needlelike monochrome oxy-carbonic acid cerium $\text{Ce}_2\text{O}(\text{CO}_3)_2$ and H_2O 1700g were obtained. This was calcinated at 400 degrees C for 2 hours, and the second cerium of oxidation was obtained. The value from which the property of the second cerium of oxidation and this second cerium of oxidation which were obtained were re-calcinated at 800 degrees C for 5 hours, and specific surface area changed is shown in Table 1.

[0011] In addition, whenever [yellow / which was shown all over Table 1] (YI value) is the value which is the following, and was made and measured. Whenever [yellow] shows the degree separated from white in the direction of yellow, and, as for ideal white, whenever [yellow] is set to about 0. The numeric value of whenever [yellow] becomes large as yellow increases and it keeps away from ideal white. On the occasion of measurement of whenever [yellow], the obtained baking object is cracked by the nylon pot (nylon ball) for about 2 hours, and it is made powder 22 micrometers or less by mean-particle-diameter

d50=2.0**0.2micrometer. 5g of this crack **** is packed and measured by no pressurizing in a round-head cel (30mm phix15t) with the Tokyo Denshoku Co., Ltd. make and a color difference meter, each value of XYZ is measured, and it is ASTM. E YI value (whenever [yellow]) was calculated according to 313. 3 times per one sample, YI value shown in Table 1 repeated the above-mentioned actuation, measured it 3 times each, and was expressed as a total of 9 times of the averages.

[0012] In example of comparison 1 example 1, humidification desiccation processing of the precipitate of a carbonic acid cerium was not carried out, but it calcinated at 400 degrees C directly for 2 hours, and the second cerium of oxidation was obtained. The other conditions are the same as an example 1. The specific-surface-area value in re-baking is shown in Table 1 for the property of the second obtained cerium of oxidation and 800 degrees C, and 5 hours.

[0013] Sediment of the hexagon-head tabular carbonic acid cerium obtained in the example of comparison 2 example 1 was put into the autoclave, and hydrothermal processing was performed at 120 degrees C for 8 hours. The main things of the obtained product were the shape of 6 corner guards, and a spherical basic carbonic acid cerium ($\text{Ce}(\text{OH})(\text{CO}_3)$ and $2\text{H}_2\text{O}$), and the amount of generation of a mono-oxy-carbonic acid cerium was about 5% of the whole. This mixture was calcinated at 400 degrees C for 2 hours, and the second cerium of oxidation shown in Table 1 was obtained. Moreover, the specific-surface-area value after re-calcinating at these 800 degrees C for 5 hours is also shown in Table 1.

[0014] Sediment of the hexagon-head tabular carbonic acid cerium obtained in the example of comparison 3 example 1 was put into the thermo hygostat of installation of steam, and 95% of relative humidity performed humidification heat-treatment at 50 degrees C for 8 hours. Consequently, the mono-oxy-carbonic acid cerium was not obtained, but was still a 6 corner-guard-like carbonic acid cerium. This was calcinated at 400 degrees C for 2 hours, and the second cerium of oxidation shown in Table 1 was obtained, and it re-calcinated at 800 more degrees C for 5 hours, and asked for change of specific surface area.

[0015]

[Table 1]

	400℃×2時間焼成後		800℃×5時間再焼成後
	比表面積(m^2/g)	Y I 値	比表面積(m^2/g)
実施例 1	153	21	15.2
比較例 1	112	32	2.7
比較例 2	112	31	2.8
比較例 3	121	28	5.7

[0016] In the example duplex ammonium-carbonate water solution, the hexagon-head tabular carbonic acid cerium was obtained on the same conditions as an example 1 except having carried out addition mixing of the cerium-nitrate water solution. The steam installation oven performed 2300g of this sediment at 95 degrees C, humidification heat-treatment was performed at 95% of relative humidity for 8 hours, and needlelike monochrome oxy-carbonic acid cerium $\text{Ce}_2\text{O}(\text{CO}_3)_2$ and H_2O 1700g were obtained. This was calcinated at 300 degrees C for 4 hours, and the second cerium of oxidation of the property shown in Table 2 was obtained. Furthermore, this is re-calcinated at 800 degrees C for 5 hours, it asks for change of specific surface area, and the value is shown in Table 2.

[0017] Humidification heat-treatment was not carried out, but the precipitate of the hexagon-head tabular carbonic acid cerium obtained in the example of comparison 4 example 2 was directly calcinated at 300 degrees C for 4 hours, the second cerium of oxidation of the property shown in Table 2 was obtained, the same re-baking processing as an example 2 was performed, and it turned out that it changes to the value of Table 2.

[0018]

[Table 2]

	300℃×4時間焼成後		800℃×5時間再焼成後
	比表面積(m ² /g)	YI値	比表面積(m ² /g)
実施例 2	161	24	13.6
比較例 4	121	34	2.8

[0019] The precipitate of the hexagon-head tabular carbonic acid cerium prepared like example 3 example 1 was put into the thermo hygostat, humidification desiccation processing was performed in 60 degrees C and 90% of relative humidity for 12 hours, and needlelike monochrome oxy-carbonic acid cerium $\text{Ce}_2\text{O}(\text{CO}_3)_2$ and $3\text{H}_2\text{O}$ 1800g were obtained. The specific surface area at the time of re-calcinating the property of the second cerium of oxidation and this second cerium of oxidation which calcinated the obtained mono-oxy-carbonic acid cerium at 500 degrees C for 2 hours, and were obtained at 800 degrees C for 5 hours is shown in Table 3.

[0020] Although the precipitate of the hexagon-head tabular carbonic acid cerium prepared like example of comparison 5 example 1 was put into the thermo hygostat and humidification desiccation processing was performed in 60 degrees C and 70% of relative humidity for 12 hours, the mono-oxy-carbonic acid cerium was not obtained, but was still a 6 corner-guard-like carbonic acid cerium. The specific surface area at the time of re-calcinating the property of the second cerium of oxidation and this second cerium of oxidation which calcinated this carbonic acid cerium at 500 degrees C for 2 hours, and were obtained at 800 degrees C for 5 hours is shown in Table 3.

[0021]

[Table 3]

	500℃×2時間焼成後		800℃×5時間再焼成後
	比表面積(m ² /g)	YI値	比表面積(m ² /g)
実施例 3	142	19	14.7
比較例 5	103	28	3.1

[0022] Sediment of the hexagon-head tabular carbonic acid cerium prepared like example 4 example 2 was put into the oven which introduced steam, humidification desiccation processing was performed in 85 degrees C and 80% of relative humidity for 8 hours, and needlelike mono-oxy-carbonic acid cerium 1700g was obtained. The specific surface area at the time of re-calcinating the property of the second cerium of oxidation and the second cerium of oxidation which calcinated obtained mono-oxy-carbonic acid cerium $\text{Ce}_2\text{O}(\text{CO}_3)_2$ and H_2O at 500 degrees C for 2 hours, and were obtained at 800 degrees C for 5 hours is shown in Table 4.

[0023] Although sediment of the hexagon-head tabular carbonic acid cerium prepared like example of comparison 6 example 2 was put into the oven which introduced steam and humidification desiccation processing was performed in 85 degrees C and 70% of relative humidity for 8 hours, the mono-oxy-carbonic acid cerium was not obtained, but was still a 6 corner-guard-like carbonic acid cerium. The specific surface area at the time of re-calcinating the property of the second cerium of oxidation and this second cerium of oxidation which calcinated this carbonic acid cerium at 500 degrees C for 2 hours, and were obtained at 800 degrees C for 5 hours is shown in Table 4.

[0024] It put into the oven which placed the bat which filled water in the pars basilaris ossis occipitalis for sediment of the hexagon-head tabular carbonic acid cerium prepared like example of comparison 7 example 2, and humidification desiccation processing was performed for 8 hours in the water vapor pressure equivalent to 110 degrees C and 85% of relative humidity. The amount of generation of the mono-oxy-carbonic acid cerium which the carbonic acid cerium which the main products in this case are hexagon-head tabular and a spherical basic carbonic acid cerium salt, in addition maintained about 20% of unreacted hexagon-head tabular is accepted, and is made into the purpose was about 5% of the whole. The specific surface area at the time of re-calcinating the property of the second cerium of oxidation and this second cerium of oxidation which calcinated the obtained mixture at 500 degrees C for 2 hours, and were obtained at 800 degrees C for 5 hours is shown in

Table 4.

[0025]

[Table 4]

	5 0 0℃×2時間焼成後		8 0 0℃×5時間再焼成後
	比表面積(m ² /g)	Y I 値	比表面積(m ² /g)
実施例 4	1 4 7	1 8	1 4 . 8
比較例 6	9 6	2 7	2 . 7
比較例 7	1 0 5	2 6	4 . 9

[0026]

[Effect of the Invention] the second cerium of oxidation obtained in this invention -- the second conventional cerium of oxidation -- comparing -- I -- there are few falls of the specific surface area in the RO high temperature which has a big specific surface area.

c) Present the color tone near white.

There is effectiveness of *****. Moreover, by the manufacture approach of this invention, the second cerium of oxidation of this invention which has the aforementioned property can be manufactured often [repeatability] and easily. Therefore, the second cerium of oxidation obtained by this invention fits especially the second cerium of oxidation with which heat-resistant stability is demanded like the catalyst for exhaust gas clarification, and a silicone rubber filler.

[Translation done.]